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## PREPARATION AND PROPERTIES OF NON-CRYSTALLINE GLASSES IN THE SYSTEM Se-I

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Vitreous  $\text{Se}_x\text{I}_{1-x}$  samples ( $x=0.1; 0.15; 0.20$ ) have been prepared and studied by thermal analysis, iodometry, X-ray diffraction and optical transmission. The results show that part of iodine remains unbonded in the structure while another part saturates the ends of selenium chains. The main effect of the iodine atoms upon the selenium matrix configuration consists in the shortening of the selenium chains and occupation of the short chain ends by atomic iodine.

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**Keywords:** Sulphur-iodine system, Iodometry, Thermogravimetry, X-ray diffraction, Optical transmission

### 1. Introduction

In 1981 Shanabrook et al. [1] reported the preparation of the first zero-dimensional solid: amorphous iodine (a-I) exhibiting one-fold coordination. The predominant inter-molecular bonding in a-I is probably a delocalized metallic-like bonding. The system Se-I is important both for the structural, specific problems of the zero-one dimensional configurations and for the control of the defects in the non-crystalline selenium with high relevance in applications.

The stoichiometric crystalline compounds  $\text{Se}_2\text{I}_2$  and  $\text{SeI}_4$  are prepared by stirring selenium with a solution of iodine in  $\text{CCl}_4$ , or selenium with a solution of  $\text{C}_2\text{H}_5\text{Br}$  [2].

We report in this paper the results on preparation and properties of several Se-I alloys in the vitreous state.

### 2. Experimental

The  $\text{Se}_x\text{I}_{1-x}$  alloys ( $x=0.1; 0.15; 0.20$ ) have been prepared by melting under vacuum in glass ampoules mixture of selenium (Hobboken 99.9999%) and iodine (Carlo Erba 99.9999%) in corresponding proportions. The ampoules were heated with the rate of  $5^\circ\text{C}/\text{min}$  up to the temperature of  $300^\circ\text{C}$  and maintained 7 hours. During the thermal treatment the ampoule was rotated with 10 turns/min. The vitreous samples were obtained by throwing the melt into water.

The samples looked grey-dark and showed a visco-plastic character immediately after preparation. The visco-plastic property decreases slowly in the interval  $1\text{-}6\text{h}$ , as a function of composition.

The optical microscopy investigations and X-ray diffraction diagrams proved the vitreous state of all the samples.

### 3. Results

#### 3.1. Iodometric results

Iodine was determined by titration with a solution of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) in presence of amidin (starch) as indicator.

It was found that not all iodine used in preparations is situated in the bonded state. For the samples  $\text{Se}_{0.8}\text{I}_{0.2}$  and  $\text{Se}_{0.85}\text{I}_{0.15}$ , after melting and rapid cooling the concentration of non-bonded iodine

is 14.86 at.% and 9 at.%, respectively. The amount of non-bonded iodine firstly decrease rapidly and after 2-3 days its amount remains practically unchanged.

### 3.2. Thermal analysis

The thermal differential analysis carried out in the interval 20-250 °C (Fig.1).

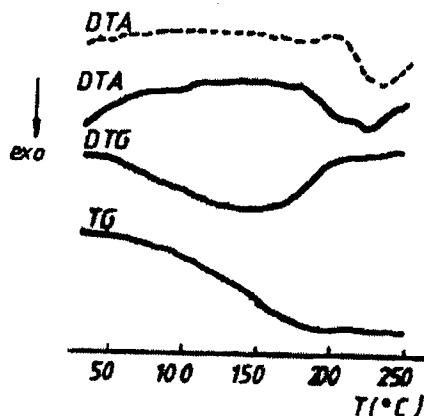


Fig. 1. DTA, DTG and TG curves for the sample  $\text{Se}_{0.8}\text{I}_{0.2}$  heating rate: 5°C/min -  $\text{Se}_{0.8}\text{I}_{0.2}$  ---Se.

Endothermal transformations are evidenced. The softening of the melts is produced in large temperature intervals (100-200 °C). The thermogravimetric curves reveal important loss of material (iodine) of the same order of magnitude as for the losses observed by iodometry measurements.

### 3.3. X-ray diffraction

X-ray diffraction patterns taken on the as-quenched samples  $\text{Se}_{0.8}\text{I}_{0.2}$  and  $\text{Se}_{0.9}\text{I}_{0.1}$ , corrected and normalized, are shown in Fig. 2.

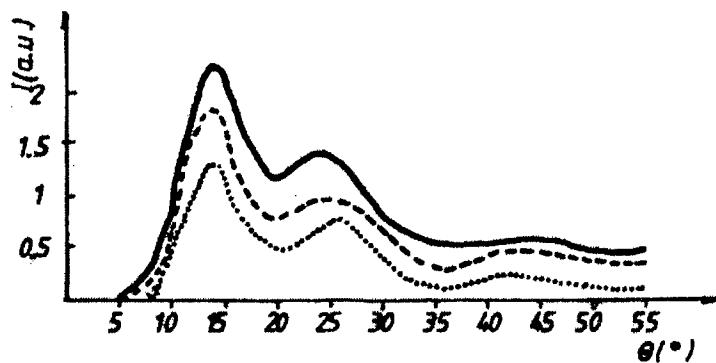


Fig. 2. X-ray scattered intensity for samples in the system Se-I.  
---  $\text{Se}_{0.9}\text{I}_{0.1}$ ; —  $\text{Se}_{0.8}\text{I}_{0.2}$ .

$\text{Cu K}_\alpha$  radiation and digital recording in the angular interval  $2\theta = 3 \div 113^\circ$  were used. The measurements were carried out in a Siemens-Kristalloflex IV diffractometer.

The reduced electron density distribution curves (REDD) are shown in figure 3.

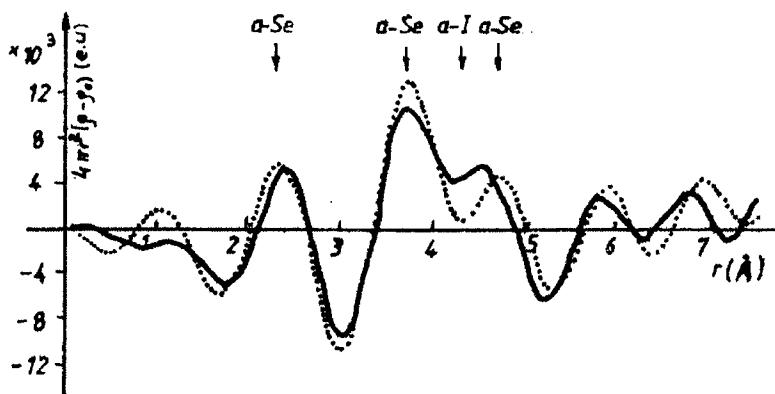


Fig. 3. REDD curves in the system Se-I.  
---  $\text{Se}_{0.9}\text{I}_{0.1}$ ; —  $\text{Se}_{0.8}\text{I}_{0.2}$ .

Careful analysis of the REDD of the vitreous samples allows to conclude that iodine strongly influence the third peak situated at  $\sim 4.5 \text{ \AA}$ . In selenium this third peak (situated at  $\sim 4.75 \text{ \AA}$ ) is related to the chain configuration. For a-Se-I the third peak shifts towards smaller  $r$  and its intensity increases when the iodine amount increases. In an old paper, Richter [3] has shown that amorphous iodine exhibits its third peak in REDD at  $4.40 \text{ \AA}$ .

### 3.4. Optical transmission spectra

Optical transmission of the vitreous Se-I samples has been recorded with a SPECTROMASTER apparatus in the infrared range ( $400 \text{ cm}^{-1}$  -  $4000 \text{ cm}^{-1}$ ). Figure 4 shows the results. For large wavelengths two absorptions peaks are evidenced for pure a-Se ( $480 \text{ cm}^{-1}$  and  $743 \text{ cm}^{-1}$ ) and they are interpreted as two-phonons and three-phonons bands of  $\text{Se}_8$ . A new absorption peak, revealed at  $\sim 860 \text{ cm}^{-1}$  in  $\text{Se}_{0.9}\text{I}_{0.1}$  is given probably by Se-I bond vibration.

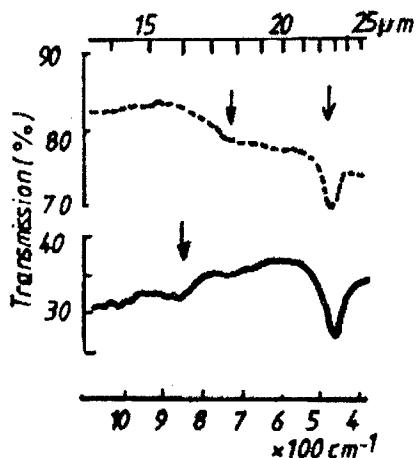


Fig. 4. Infrared transmission spectra for samples in the system Se-I.  
—  $\text{Se}_{0.9}\text{I}_{0.1}$  --- a-Se.

### 3.5. Electrical resistance

We have measured the electrical resistance of the sample with maximum amount of iodine:  $\text{Se}_{0.8}\text{I}_{0.2}$ . Two measurements were carried out. The first one was made immediately after preparation and the change of resistance in time was followed (Fig. 5a). The second one was made after 20 days of storage (Fig. 5b).

The rapid drop of the electrical resistance immediately after preparation can be due to two causes: a partial crystallization and the release of iodine. The second cause seems to prevail, because

the non-bonded iodine in fresh samples is in high amount. For long time storage, a partial crystallization is produced, as evidenced by X-ray diffraction (peaks ascribed to iodine ( $I_2$  crystallites) were revealed).

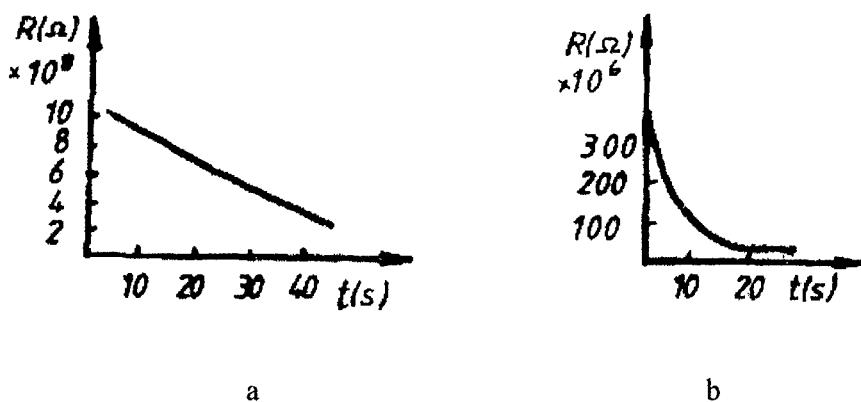


Fig. 5. The evolution of the electrical resistance in the  $Se_{0.8}I_{0.2}$  vitreous sample

- a) immediately after preparation
- b) after 20 days of storage.

#### 4. Discussion

The properties of vitreous Se-I alloys are strongly influenced by the iodine content. The fresh samples rich in iodine are not stable due to non-bonded iodine accumulated in between the selenium configurations. Selenium and iodine form a simple eutectic for 52 at%Se, with the melting temperature  $58 \pm 1^\circ C$  [4]. After Golubkova and Petrov [5] the solubility of iodine in selenium does not exceed 2 at.%.

The stabilization of the vitreous Se-I alloy is reached for low iodine content and long storage at room temperature. In this case the iodine is strongly bonded with selenium. Klapötke and Passmore [6] succeeded to prepare a number of salts of selenium iodine cations, all of which contain covalent Se-I bonds. The average selenium-iodine bond distance is  $2.51 \text{ \AA}$  and is near to the sum of the covalent radii of Se and I ( $2.493 \text{ \AA}$ ). The existence and stability of selenium-iodine cations suggest the possibility to find such configurations in vitreous Se-I. Because the structure of Se-I may be thought as a disordered packing of selenium chains, with iodine occupying the positions at the end of these chains, the iodine doping may be useful for the investigation and control of the defect states in non-crystalline selenium.

#### 5. Conclusions

The properties of Se-I glassy are determined by the iodine content. Part of iodine is bonded to the ends of selenium chains while the other part (molecular  $I_2$ ) can be released spontaneously (at room temperature) or by heating. A minimum amount of iodine cannot be eliminated and, therefore, only Se-I alloys poor in iodine are convenient in applications.

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